CONVERSION OF HIGH LEVEL WASTE TO CHLORIDE FOR PYROMETALLURGICAL PARTITIONING OF MINOR ACTINIDES

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ABSTRACT

A pyrometallurgical partitioning process is being developed for recovering minor actinides from high level wastes of PUREX reprocessing. Since the high level wastes consist of concentrated raffinates, concentrated alkaline wastes and insoluble residues, various elements contained in the wastes must be converted to the chloride form before supplied to the pyrometallurgical partitioning process. The conversion to chloride is carried out in the combination of denitration and chlorination. The material balance of the processes was measured in the present study using the simulated high level waste containing 18 elements. The results indicated that almost all of alkali elements and Re, substituting for Tc, and significant amounts of Se, Cr, and Mo were separated in denitration, and that Se, Cr, Fe, Zr, Mo, and Te in chlorination. Noble metals, Ni, alkaline-earth, and rare-earth elements, thus remained, were efficiently converted to the chloride, which is then supplied to the reductive extraction test using a molten salt / liquid Cd system in order to demonstrate that the chloride obtained is suitable for the pyrometallurgical partitioning process. Of further reduction, noble metals and Ni were reduced and extracted into the liquid Cd phase, more than 99% of rare-earth elements into the liquid Cd phase by the addition of Li reductant, and those elements were then separated from alkaline-earth elements remained in the chloride phase. Because of the chemical similarity of actinides to rare-earth elements, actinides are considered to behave as well as rare-earth elements in those test conditions.

INTRODUCTION

Nuclear energy is the most promising option for future generations when considering the global environmental protection. Before the future deployment of the nuclear energy in the global scale, the management of high level wastes (HLW) is one of the most important problems to be solved urgently. Since HLW contains several long-lived radioactive nuclides, the potential hazard of HLW due to radio-toxicity is predicted to be maintained more than several million years. Minor actinides (MA), such as Np, Am, and Cm, contribute mainly to the potential hazard after the period of approximate 100 years elapsed after the reprocessing of spent fuels. If MA could be separated from HLW and transmuted to short-lived nuclides, not only would nuclear waste management be much simpler but to obtain the public support for the nuclear power generation easier.

In 1988, Japan Atomic Energy Commission substituted a report entitled "Long Term Program for Research and Development on Nuclide Partitioning and Transmutation (P-T) Technology". The R&D program is named "OMEGA", the acronym derived from "Options Making Extra Gains from Actinides and fission products (1). In the frame of OMEGA program, the studies on the pyrometallurgical partitioning of long-lived radioactive nuclides from HLW have been carried out in our laboratory (2).

The pyrometallurgical partitioning process (pyro-partitioning) has following benefits as compared with conventional aqueous processes. The pyro-partitioning is expected to (I) generate less secondary radioactive wastes, because the degradation of inorganic solvent, reductant, and reaction gas used in the pyro-partitioning is less significant than that of organic material in the aqueous processes, and because the inorganic materials are capable of recycling, (II) favor much compact facilities, (III) control the criticality in the process easier, etc. The product purity is, on the other hand, lower in the pyro-partitioning than the aqueous processes, corresponding that a small amount of impurities,

especially rare-earth elements (RE), might be accompanied with MA, when the pyro-partitioning is applied for the treatment of MA. However, the accompaniment of a comparable RE weight with MA is allowed for the MA transmutation when the transmutation is carried out in metallic fuel fast reactors (3).

Figure 1 indicates the flow diagram of the pyro-partitioning (4). The various elements contained in HLW is firstly dehydrated and denitrated to the oxide form by heating in a denitration step and then converted to the chloride form by reacting with chlorine gas in an LiCl-KCl eutectic salt bath in a chlorination step. Those two steps are called a pre-treatment process. Since alkali nitrates is stable and not denitrated in the denitration condition that the denitration temperature is controlled around 773K or lower, alkali elements are roughly separated from the other oxide by rinsing with water after the denitration. The rough separation of Fe, Zr, and Mo might be carried out in the chlorination step based on the high volatility of the chlorides. The chlorides recovered in the salt bath are supplied to the pyro-partitioning that consists of (I) reductive extraction for the separation of noble metals and (II) multistage extraction for the separation of alkaline-earth elements and RE. The reductive extraction is carried out in a molten chloride / liquid Cd system, based on the difference of the formation Gibbs energy for chlorides in the molten chloride phase and the solution Gibbs energy for solute metals in the liquid Cd phase. The nobler elements than U are recovered into the liquid Cd phase by adding Li reductant. The molten chloride phase is then supplied to multistage extraction step, where actinides are selectively reduced and extracted into the liquid Bi phase by adding Li reductant in a molten chloride / liquid Bi system, whereas alkaline-earth elements and RE are remained in the molten chloride phase. In the spent chloride treatment step, alkaline-earth elements and RE are recovered into a lead electrode by electrolysis of the chlorides. Chlorine gas and LiCl-KCl generated in the step are recycled back to the chlorination step.
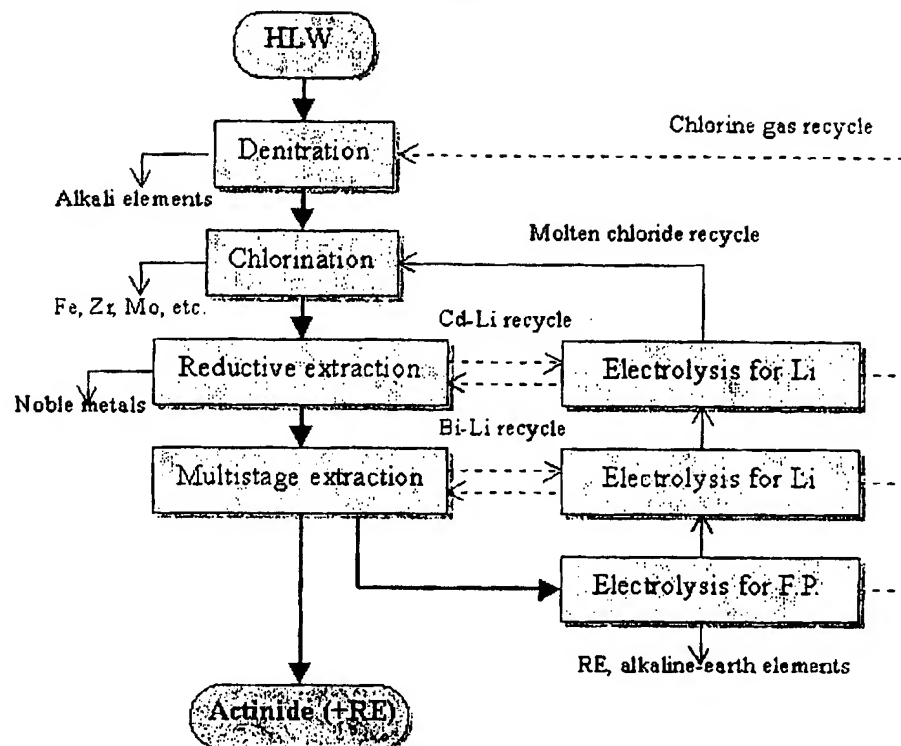
Fig. 1.   Flow diagram of pyro-partitioning process.

The basic thermodynamic data related to each step have been measured (3,4,5,6) and the demonstration tests of each step have been also promoted by using simulated materials (4,7,8). The both results certified the feasibility of each step of the pyro-partitioning. Two kinds of continuous test was planed to demonstrate the feasibility of the whole process. Present study focused on the continuous demonstration test from denitration to reductive extraction using a simulated HLW as an initial input. Since the behavior of actinides is similar to RE in the test conditions, RE was used to substitute for actinides. Another demonstration test was carried out from reductive extraction to multistage extraction using simulated mixed chloride reagents containing MA, which is described in detail in elsewhere (9).

EXPERIMENTAL

Denitration

The simulated HLW was prepared from nitrate reagents of 18 elements. The concentration of each element corresponded to the sum of concentrated raffinates, concentrated alkaline wastes, insoluble residues, and corrosion products of claddings, as indicated in Table 1. Those values are based on the calculation using ORIGEN-II code. To simplify the analysis, Cs and Ba represented to alkali and alkaline-earth elements, respectively, and Y, Ce, Nd, and Sm to RE. Re is used to substitute for Tc. Since the amount of Ag, Sn, Cd, and other F.P. in HLW is much smaller than the elements described in Table 1, those elements were not used in the present study. For the acidity, $2N\text{-}HNO_3$ was chosen as simulating the HLW condition. In those concentrated solution, some elements were not completely dissolved in the nitric acid. Therefore, we prepared two samples in the same manner

and one sample was completely dissolved in aqua resin to determine the initial amount of each element.

Figure 2 (a) illustrates the apparatus for the denitration test. The simulated HLW, 100 ml in volume, was prepared in a stainless-steel crucible. It was heated at 373K for 1 hour in an air atmosphere to volatilize water and a surplus of nitric acid. Then, the sample was heated at 773K for 1 hour to decompose the various nitrates except for alkali elements. At that temperature, alkali nitrates formed a stable molten nitrate and the compatibility between alkali molten nitrate and the stainless-steel crucible was excellent. Therefore, the stainless-steel is adequate for denitration crucible. A 3N-KOH trap was attached in an off-gas line to recover volatilized materials. The denitrated sample was cooled to room temperature and then rinsed with water to recover water-soluble alkali nitrate in the aqua phase. The oxides recovered with a centrifugal separator were calcinated at 773K for 1 hour. Approximate 1 g of sample was taken before and after the calcination respectively to measure the material balance and to investigate the chemical form. Quantitative analysis was carried out with ICP-AES and the chemical form was determined from the X-ray diffraction patterns. The rest of the sample, approximate 8 g in weight, was supplied to the following chlorination test.

Chlorination

The chlorination test was carried out in a purified Ar atmosphere glove box. Figure 2 (b) schematically shows the apparatus for chlorination. The denitrated sample was introduced in a pyro-graphite crucible, 80 mm in diameter and 120 mm in height, with approximate 50 g of LiCl-KCl eutectic chloride. Pyro-graphite is selected due to the compatibility with chlorine gas. It was heated at 973K to melt, and then chlorine gas, 100

TABLE I
Concentration and Composition of 18 Elements in Simulated HLW

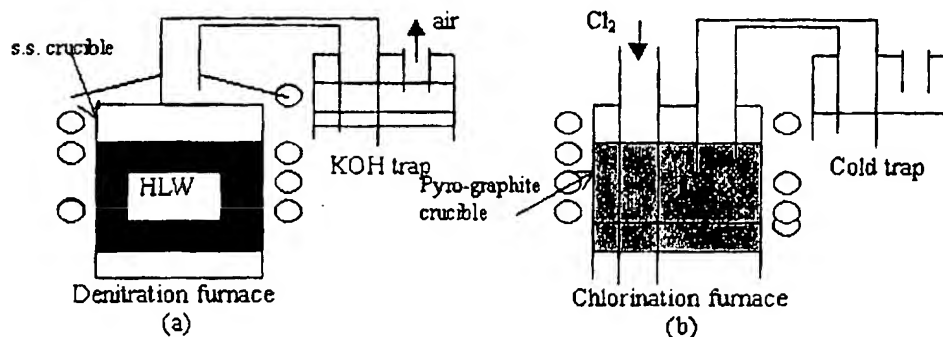| Element	Concentration in sim. HLW (g/l)	Composition of cation (at.%)	Element	Concentration in sim. HLW (g/l)	Composition of cation (at.%)
Na	26.589	58.57	Re*	4.148	1.13
Cs	9.050	3.45	Ru	5.748	2.88
Ba	7.088	2.61	Rh	1.238	0.61
Y	1.634	0.93	Pd	4.998	2.38
Ce	10.593	3.83	Fe	4.827	4.38
Nd	12.531	4.40	Cr	0.893	0.87
Sm	2.803	0.94	Ni	1.718	1.48
Zr	10.133	5.63	Se	0.157	0.10
Mo	9.900	5.23	Te	1.485	0.59

* Re substitutes for Tc.

Fig. 2. Experimental apparatus for (a) denitration and (b) chlorination tests.

cc/min. in rate, was introduced for 14 hours in the molten chloride through a graphite tube, 4mm in diameter. The molten chloride was then cooled to room temperature and approximate 7 g of chloride was sampled after crushing and mixing. The obtained chloride sample was dissolved in water to recover water-soluble chlorides. Water-insoluble oxides or oxychlorides that contained partly in the sample was then filtered. The quantitative analysis of the both water-soluble and filtered samples was carried out with ICP-AES. Since some chlorides were volatilized during chlorination, they were collected in a cold trap attached in an off-gas line. The volatilized amounts of each element were measured from the analysis of trapped materials.

Reductive Extraction

Approximate 15 g of chloride sample obtained in the chlorination test was supplied to the reductive extraction test. The chloride was melted in an alumina crucible, 25 mm in diameter, at 773K. Approximate 5g of Cd was added to the molten chloride and then maintained at 773K for a day. After noble metals were extracted into the Cd phase, approximate 0.5 g of the chloride phase was sampled to measure the composition. Then the chloride and Cd melts were poured respectively out of the crucible on the stainless steel plates. The surface of the recovered Cd sample was washed with water to remove chlorides thoroughly, and then the Cd sample was dissolved in nitric acid for the quantitative analysis.

In order to certify the applicability of the chloride after the reductive extraction to the multistage reduction, the following test was carried out. The recovered chloride was re-melted in the alumina crucible at 773K. Small amounts of Cd-Li alloys were incrementally added in the melt with the interval of approximate 8 hours. In advance of each addition of the Cd-Li alloys, approximate 0.3 g of the chloride phase was sampled to measure the change of the chloride composition. Although the use of liquid Bi was proposed for the multistage extraction of the pyro-partitioning (4), liquid Cd was used in the present study instead of Bi. However, the previous study (5) indicated that the separation capability of RE and actinides from alkaline-earth elements in the molten chloride / liquid Cd system is almost equal to that in the molten chloride / liquid Bi system. After the RE amounts in the chloride phase decreased to approximate 1% with respect to the initial amounts, the chloride and Cd melts were poured respectively out of the crucible on the stainless steel plates. The quantitative analysis was respectively carried out for the water-soluble chloride part in the chloride melt, water-insoluble oxide or oxychloride part in the chloride melt, and the Cd melt.

RESULTS AND DISCCUSSION

Denitration and chlorination

Figure 3 indicates the material balance with respect to the initial amount of each element after the pre-treatment process. The material balance was summarized into a) volatilized ratio in denitration, b) remained ratio as oxides or oxychlorides in chlorination, c) recovered ratio in the aqua phase in denitration, d) volatilized ratio in chlorination, and e) recovered ratio as chlorides in the molten salt bath in chlorination. The values for a), c), and d) were directly obtained from the analytical values. The values for b) and e) was calculated from the analysis of sampling materials after chlorination. The deviations of the total mass bal-

ance from the initial 100% value for each element except for Tc and Ru are within 5% that is considered to be within the analytical error of ICP-AES. The sum of Te amount detected was 108% with respect to the initial 100% value. The Ru mass balance remained only 76%. The rest of Ru is considered to be volatilized and not captured in the KOH trap. According to an additional denitration experiment using a 1N-HNO$_3$ trap instead of a 3N-KOH trap, approximate 20% and 80% of Ru with respect to the initial amounts were detected in the trap and stainless steel crucible, respectively.
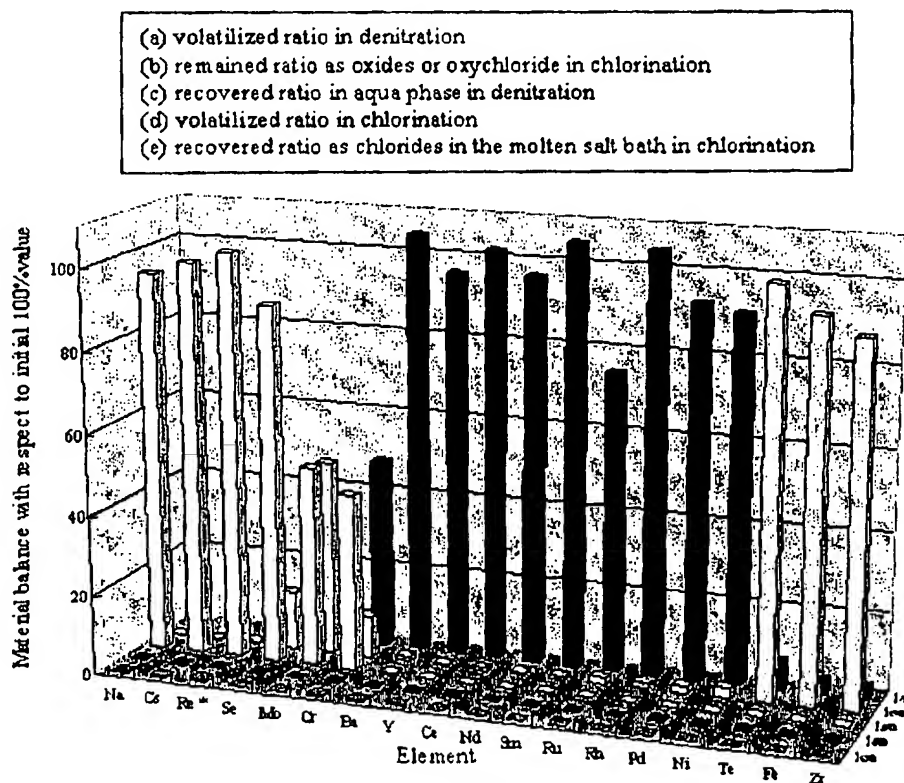
More than 98% of Na, Cs, and Re with respect to the detected amounts were recovered in the aqua phase in the condition that no significant volatilization occurred except for Ru. The Significant amounts of Se, Mo, and Cr were also detected in the aqua phase. Those elements were supposed to be dissolved in the aqua phase by forming the double oxides with alkali elements, which is confirmed from the following analysis. The nitrate anions in the aqua phase were measured with ion-chromatography, resulting that the nitrate anions remained as much as 94.5% of detected alkali element cations. Assumptions that a part of alkali elements formed the double oxides with a part of Se, Mo, and Cr and that the double oxides were dissolved in water corresponded to the decrease by approximate 7.5% in nitrate amounts. This value almost agreed with the difference between the detected nitrate and alkali element amounts.

In chlorination, 97%, 96%, and 93% of Zr, Fe, and Te, respectively, with respect to the detected amounts were volatilized and recovered in the cold trap. Almost all of the rest of Se and Mo was also captured in the trap. Furthermore, the volatilization ratios for noble metals and Ni were approximate 2% except for Rh and those for alkali and alkaline-earth elements, and RE were remained lower than 1%. Therefore, almost all of RE, Rh, Pd, and Ni chlorides were supplied to reductive extraction with the significant amounts of Cr and Ru and the small amounts of the other chlorides.

Reductive Extraction

Figure 4 indicates the material balance of 15 elements during reductive extraction operations with respect to the values contained in the chloride supplied. Since the amounts of Se, Te, and Re in the chlorinated sample were near the detection limit of ICP-AES, the analysis for those elements was not promoted. The deviations of the total mass balance from the initial 100% values for noble metals, RE, Ni, Zr, Na, and Ba were within 5%. Although the deviations for Fe, Mo, and Cs attained +14%, -17%, and -17%, respectively, it was originated from the fact that the amounts supplied for reductive extraction were extremely low.

More than 99% of noble metals and Ni with respect to the detected total amounts were selectively recovered in the Cd phase without the addition of Li. Although Fe should be reduced and Zr not reduced according to thermodynamic data, 36% of Fe

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> (a) volatilized ratio in denitration
> (b) remained ratio as oxides or oxychloride in chlorination
> (c) recovered ratio in aqua phase in denitration
> (d) volatilized ratio in chlorination
> (e) recovered ratio as chlorides in the molten salt bath in chlorination

* Re substitutes for Tc.

Fig. 3.   Material balance of 18 elements with respect to initial 100% value in denitration and chlorination tests.

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(a) remained ratios as residues after reductive extraction
(b) extracted ratios in Cd
(c) extracted ratios in Cd by adding Cd-Li
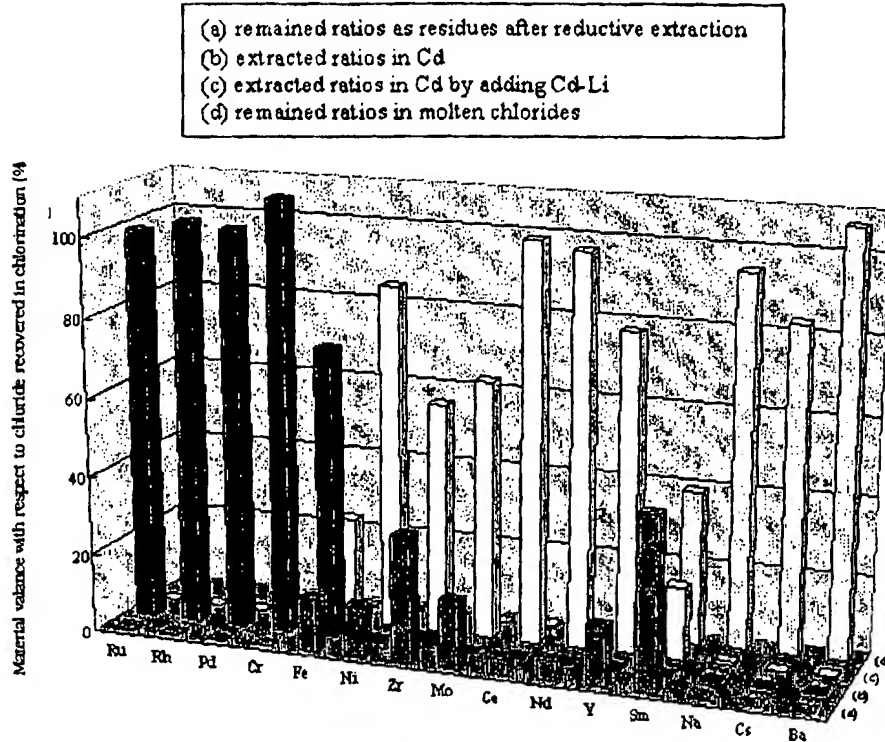(d) remained ratios in molten chlorides

Fig. 4.   Material balance for 15 elements with respect to the 100% value contained in the chloride
supplied from chlorination during reductive extraction test.

was not reduced and 3% of Zr reduced. This phenomena might be due to the formation of the intermetallic compounds among the elements in the Cd phase. By adding Cd-Li alloys, more than 99% of Ce and Nd were removed from the chloride phase, accompanying with 100% of Ni and Mo, 97% of Zr, 96% of Y, 61%of Sm, 36% of Fe, and small amounts of other elements. However, significant amounts of those elements were not recovered in the Cd phase, but formed the third phase. The chemical morphology for the third phase was not elucidated. Since the elements recovered by the addition of Cd-Li alloys were considered to react with oxygen impurities in the system, the recovered ratios for RE in the Cd phase might increase with decreasing the impurities. Almost all of Ba and alkali elements as well as 39% of Sm and 4% of Y remained in the chloride and separated from other elements.

CONCLUSION

Material balance of the pretreatment process for the pyro-partitioning was measured using simulated HLW containing 18 elements, resulting that (I) significant amounts of alkali elements, Re, Se, Cr, and Mo were separated in denitration and (II) those of Fe, Cr, Mo, and Te in chlorination. Material balance of the reductive extraction step was also measured using the chlorides recovered in the pretreatment process for simulated HLW, resulting that (I) noble metals were selectively separated into the

Cd phase without the addition of Cd-Li, (II) Ni and RE, substituting for actinides, by the addition of Cd-Li, and (III) alkaline-earth elements remained in the chloride phase. Those results indicated that the pretreatment process described in the present study is capable for the rough separation and that the chloride recovered in the pretreatment process is suitable for the pyro-partitioning process.

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